(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 522 776 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification : **03.08.94 Bulletin 94/31**

(51) Int. Cl.[5] : **B01J 4/00,** B01J 19/24, B01J 19/26, C08G 77/06

(21) Application number : **92306051.1**

(22) Date of filing : **30.06.92**

(54) Polymerisation reactor and polymerisation process.

(30) Priority : **12.07.91 GB 9115170**

(43) Date of publication of application : **13.01.93 Bulletin 93/02**

(45) Publication of the grant of the patent : **03.08.94 Bulletin 94/31**

(84) Designated Contracting States : **AT BE CH DE ES FR GB IT LI NL SE**

(56) References cited :
FR-A- 2 015 980
US-A- 3 434 805
US-A- 4 855 112
PATENT ABSTRACTS OF JAPAN vol. 9, no. 175 (C-292)(1898) 19 July 1985

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Description

This invention relates to a polymerisation reactor for making liquid polymers. It is particularly related to static reactors, more specifically those which are useful in the polymerisation of monomers or oligomers through condensation reactions. The invention also relates to a process of making liquid polymers.

Polymerisation reactors have been known for a long time and have been used for a variety of polymerisation processes. Reactors may be suitable for batch operation or continuous operation. The present invention is concerned with the latter type. Most of the current continuous polymerisation reactors are dynamic systems having some moving parts which effect mixing of the reagents and, where necessary the catalyst, and which force the reaction mixture through the reactor. Many continuous polymerisation units comprise tubular systems using appropriate mixing means. Dynamic reactors also require a fair amount of maintenance and are subject to potential breakdown of the mechanism. Static continuous reactors, where no moving parts are used to force the reaction mixture through the reactor, are also known. Adequate mixing in these reactors is mostly achieved through adapted internal geometry and/or the presence of internal parts, e.g. baffles, in the construction of the reactor.

In existing continuous reactors the residence time of the reagents may be quite extended, especially where efficient distribution of a catalyst and heat transfer are critical. In many systems there is also a danger that the polymer will build up on the walls of the reactor, thus reducing the efficiency of the unit and fouling the reactor. Build-up on the walls often requires shutting down of the polymerisation equipment and expensive labour in order to clean the build-up of polymers from the reactor walls. Numerous solutions have been suggested, but there is still a need to provide a polymerisation process which will allow the formation of polymers in an improved manner by using an efficient static reactor.

We have now found that it is possible to improve the polymerisation process and reduce the build-up of high viscosity liquid polymers on the walls of the reactor, by providing porous walls inside at least part of the reactor and backflushing, i.e. passing a fluid through said walls in the reactor.

The use of a porous wall in polymerisation reactors has been disclosed in Japanese Patent 60-47030. In said specification it is stated that as in condensation polymerisation, especially in the latter stages thereof, removal of the products of the condensation reaction is rate determining, the polymerisation rate is increased by carrying out the polymerisation in the form of a thin film. The specification addresses the problem of improving such thin film polymerisation. The proposed solution is the provision of a porous material body, through which an inactive gas can pass, inside a heated reaction vessel. The initial condensate is then passed in the form of a layer on the outer surface of the porous material body, and an inactive gas is passed through the porous material body and introduced into the layer of initial condensate to undergo condensation polymerisation. By using this method there is stated to be no need for any motive power to agitate a highly viscous material, or for maintaining a high vacuum system, and moreover, removal of the condensation product is facilitated by the introduction of the inactive gas into the initial condensate and foaming.

The Japanese application only relates to thin film polymerisation systems. Such systems require very large surface areas to achieve commercially acceptable output rates. There is no indication of any use for such system outside thin film polymerisation. Neither is there any indication how to solve the problem of build-up of high viscosity materials on the walls of a reactor. There remains a need to provide a static reactor which is able to give improved polymerisation, avoiding the build-up of polymers on the reactor walls and which is not restricted to the thin-film polymerisation systems.

According to the present invention there is provided a continuous static polymerisation reactor for the production of liquid polymers, which comprises an inlet means, said inlet means comprising an atomising device an elongated hollow reaction chamber, having a porous wall, a jacket means spaced from and in surrounding relationship to said porous wall, means for introducing a fluid through the porous wall into the elongated hollow reaction chamber and an outlet means.

The inlet means of the polymerisation reactor may be provided with a means of feeding the reagents under pressure. For example, the inlet means may be provided with a pumping system to feed the reaction mixture under pressure, e.g. from a container placed at some distance from the inlet means. Another method is the feeding under gravity. The feeding means may cause the reagents to pass through a heating mechanism which will allow the reagents to be brought to a higher temperature, e.g. the reaction temperature. Where a catalyst is required, the feeding means may also include a mixing device for mixing the reagents and the catalyst at the right proportions.

In a preferred embodiment the reaction mixture is mixed with a pressurised gas at the inlet means, the gas being used to force the reaction mixture through the reaction chamber of the polymerisation reactor. This pressurised gas may be any inert gas, e.g. air or nitrogen. In this preferred embodiment the mixing in of the gas with the reaction mixture is effected in a way which will cause the reaction mixture to reach a foam-like

consistency. In this way a large air liquid interface is created, making the system especially useful for polymerisation reactions which are of the condensation polymerisation type, i.e. where water or another simple material is formed as a by-product from the reaction of two monomers or oligomers.

The inlet means is provided with an atomiser. Where pressurised gas is used some of the gas may be employed to aid the atomisation of the reaction mixture. Atomisers are well known in the art. The mixture may be atomised by conventional means. This includes the pressurising of the reaction mixture through an atomising device causing it to form a spray of small particles. An alternative, and more commonly used, method is the use of a pressurised gas, e.g. compressed air or nitrogen, to atomise the reaction mixture when it passes through the device. This is often referred to as the 2-fluid nozzle system. Also commonly used is the so-called rotary atomiser which causes the reaction mixture to form small droplets by feeding it onto a fast rotating plate. Where the reaction mixture is atomised, the additional use of pressurised gas and the narrowness of the reaction chamber into which the mixture is fed causes the composition to reach a foam-like consistency in which all ingredients are exceptionally well dispersion and mixed. Efficient mixing becomes very important where small amounts of catalyst are used in the polymerisation reaction. The reaction mixture may be brought to increased temperature by heating the mixture itself prior to the inlet means. Alternatively, or additionally, the mixture may be heated by using heated pressurised gas or by heating the reaction chamber into which the mixture is fed.

The reaction chamber is elongated and hollow to receive the reaction mixture. It is preferred that the reaction chamber is of cylindrical shape, although this is not necessary. Cylindrical chambers are easier to manufacture and have a geometry which is more favourable for good mixing, eliminating any possible dead space. With the expression elongate, is meant that the length of the chamber in the direction of flow of the reaction mixture is at least twice the diameter of the chamber at its widest point. Preferably the diameter of the reaction chamber is from 2 to 25cm, more preferably from 5 to 10cm. Larger diameters are also possible, but will only be efficient if sufficient reaction mixture is provided to cause sufficient flow in the reactor to ensure efficient mixing and heat transfer in the reaction mixture. Adequate rates for such diameters would be impracticable in most cases. The length of the reaction chamber will depend on the flow rate of the reaction mixture, the efficiency of the catalyst and other rate determining factors. A suitable length of reactor chamber would be from 25cm to 20 metres, more preferably from 50cm to 10 metres, most preferably 2 to 8 metres. It is preferred to have a reaction chamber of such dimensions that the reaction mixture will have a residence time in the reaction chamber of less than 5 minutes, preferably less than 2 minutes. A particularly useful reaction chamber, for example for the production of up to 200kg of polymer per hour, would be about 4 metres in length with an internal diameter of about 5cm. The chamber may be an elongate tube, which is substantially straight, or it may be coiled or in any other way shaped. A coiled reaction chamber has the advantage or reducing the required overall length or height of the reactor. The characterising feature of the reaction chamber is that it is equipped with a porous wall. In the most preferred embodiment the complete wall of the reaction chamber is porous, although it may be envisaged that certain portions thereof are not porous, e.g. parts which are used for fixing the reactor chamber in place or for attaching the jacket means. The porosity of the wall has to be sufficient to enable a fluid material to be fed though the wall into the reaction chamber. Where the fluid is a pressurised gas the requirement for porosity will be lower than where a liquid material is fed through. Preferably the porosity is sufficient to allow liquid material to pass through, e.g low or medium molecular weight oligomers or monomers, which may then take part in the polymerisation reaction. The porous wall in the reaction chamber may be made of any suitable material, which is itself inert to the polymerisation reaction. Suitable materials for making the porous wall include sintered porous plastic, e.g. polyethylene or polypropylene, sintered ceramic, sintered glass or microporous metal. Preferably the permeability of the porous wall is in the region of from 2 to 70 nanoperms, e.g 20 nanoperms. (1 nanoperm = 10^{-13} m^2)

By virtue of the mixing system or atomising system which is used to feed the reaction mixture into the reaction chamber, and by the use of pressurised gas to force the mixture through the reactor, sufficient turbulence is created to ensure efficient polymerisation of the monomers and/or oligomers.

The porous wall of the reaction chamber is surrounded by a jacket means which is spaced from the porous wall so as to form a cavity around the porous wall. This jacket means may take the shape of the reaction chamber, and thus be elongate, preferably cylindrical in shape. Alternatively the jacket means may be a cuboid or short cylindrical shape inside which the reaction chamber is placed, e.g. where the latter is coiled, as referred to above. The jacket means may be made of any suitable material provided it is itself impermeable to the fluid which is used to be fed through the porous wall. Suitable materials include galvanised or stainless steel, glass, plastic or enamelled metal. The jacket means may be provided with a heating facility if desired.

The jacket means has connected to it a means for introducing a fluid through the porous wall. This may be in the form of a pump or other pressurising system, e.g. a source of compressed air. Where a reaction chamber of substantial length is used it may prove beneficial to have the jacket means split into several sections,

each section providing the fluid at a different pressure, in order to adjust to the decreasing pressure which is present inside the reaction chamber when moving further from the inlet means. It is even possible to provide a plurality of jacket means, each adapted to introduce a different fluid into different parts of the reaction chamber if so desired. Only sufficient fluid needs to be introduced to avoid build-up of the polymer on the inside of the reactor wall. Where the fluid is a gas this may contribute to the formation of a foam-like consistency, increasing the surface area of the interface. Where the fluid is a liquid this liquid will be mixed into the reaction mixture. Depending on the nature of the liquid, it may co-react or it may be used as a diluent or solvent for the reaction mixture.

The polymerisation reactor also has an outlet means, most suitably the open end of the reaction chamber. There the polymerised liquid material may be collected immediately in a suitable receptacle, e.g. drum. It is possible to pass the polymer through a de-aeration system, especially in the preferred reactor where a mixture with foam-like consistency was formed to pass through the reaction chamber. Where there is a need to neutralise the catalyst, the collection point may be linked to a duct into which a neutralisation agent is added and mixed at the appropriate ratio. A cooling system may also be installed at or near the collection point, in order to bring the polymer to the desired temperature. A filtration system may be employed, e.g. to filter out any salts formed by neutralisation of the catalyst. Usually a filtration system will be installed before a cooling device as it is easier to filter a hot liquid which has a lower viscosity.

The reactor in which pressurised gas is used to reach a foam-like consistency is particularly useful for the manufacture of liquid polymers by condensation of oligomers and/or monomers.

According to another aspect of the invention there is provided a process for making liquid polymers by condensing monomers and/or oligomers in a polymerisation reactor, comprising the mixing of the monomers and/or oligomers with the appropriate amount of catalyst where required, the mixing of the resultant mixture with a pressurised gas to cause it to reach a foam-like consistency, feeding the foaming mixture through an inlet means into a reaction chamber having a porous wall, feeding a fluid through the porous wall into the reaction chamber in order to avoid build-up of the polymer on the wall of the reaction chamber, causing the monomers and/or oligomers to polymerise in the reaction chamber and collecting the polymers at the outlet means of the polymerisation reactor.

The term 'liquid', where herein used in relation to polymers, monomers or oligomers, denotes the type of materials which have a consistency which will allow them to flow at a temperature of 25°C and adapt to the shape of the receptacle in which they are placed when submitted to a pressure, e.g. gravity. For the sake of clarity it is hereby stated that liquid materials excludes those materials which are clearly solid or clearly gaseous and those materials which are thermoplastic. For example, the term 'liquid polymers' includes apart from low viscosity polymers, e.g. those having a viscosity of 20 mm^2/s, also those polymers which have a high viscosity, e.g. gum-like materials and some very loosely crosslinked materials, e.g. certain gels, which will flow under pressure.

The process is limited to those polymers which are made by the condensation reaction of monomers and/or oligomers. With condensation is meant the chemical reaction in which two or more molecules combine, with the separation of water or some other simple substance, as defined in ASTM D883-54T. The process of the invention is particularly useful for the condensation polymerisation because a large surface area is created at the gas liquid interface. This encourages the by-product of the condensation reaction, e.g. the water, to migrate into the gas phase, especially when the temperature in the reaction chamber is sufficiently high to volatilise the said byproduct. This will force the equilibrium of the reaction towards the condensation polymerisation, thus speeding up the polymerisation reaction. A typical example of a condensation reaction is an ester formation by reacting a carboxylic acid with an alcohol, or the formation of an ether by the reaction of two alcohols, both reactions liberating water. One particular condensation polymerisation reaction which is suitable for the process of the present invention is the formation of polysiloxane materials by condensation of organosilicon compounds having silanol groups.

The process of the invention is particularly preferred for the manufacture of organosiloxane materials by polymerisation of organosilicon compounds having silicon-bonded -OR radicals, in which R represents a hydrogen atom or a lower alkyl group having up to 6 carbon atoms provided at least some of the R groups are hydrogen atoms. It is most preferred that each R group represents a hydrogen atom.

Organosilicon compounds, forming the monomers or oligomers in the process of the invention, may be organosilanes, organosiloxanes, silcarbanes or mixtures of two or more of these. The silicon-bonded organic substituents in the organosilicon compound may be monovalent hydrocarbon groups having from 1 to 14 carbon atoms, for example alkyl, aryl, aralkyl, alkaryl or alkenyl groups or monovalent substituted hydrocarbon groups having from 1 to 10 carbon atoms, for example amino-substituted alkyl or aryl groups, mercaptoalkyl groups, haloalkyl groups, esterified carboxyalkyl groups, polyoxyalkylene groups and hydroxyalkyl groups. Specific examples of suitable organic substituents which may be present in the organosilicon compounds em-

ployed in the process of the invention are methyl, ethyl, propyl, hexyl, dodecyl, tetradecyl, phenyl, xylyl, tolyl, phenylethyl, vinyl, allyl, hexenyl, $-R'NH_2$, $-R'NHCH_2CH_2NH_2$, -R'SH, -R'Br, -R'Cl and R'OH, wherein R' represents a divalent organic group, preferably having less than 8 carbon atoms, for example $-(CH_2)_3-$ or $-CH_2CHCH_3CH_2-$, arylene, e.g. $-C_6H_4-$ or aralkylene, e.g. $-(C_6H_3.CH_3)-$. For the majority of commercial applications at least 50% of the organic substituents will be methyl groups, any remaining groups being selected from vinyl and phenyl groups. More preferably at least 80% of all organic substituents are methyl groups, most preferably, substantially all organic substituents.

Although organosilicon compounds for use in the process of the invention may have a number of silicon-bonded groups -OR per molecule, it is preferred that no more than two -OR groups are present on each molecule. This will encourage the formation of substantially linear polysiloxane materials. The preferred organosilicon compounds are short chain linear polydiorganosiloxane materials having silanol end-groups. These materials have the average general formula

$$HO-\underset{R''}{\overset{R''}{\underset{|}{\overset{|}{Si}}}}\left[-O\underset{R''}{\overset{R''}{\underset{|}{\overset{|}{Si}}}}-\right]_n OH$$

wherein each R" denotes an organic group as hereinabove described and $\underline{n}$ is an integer, preferably having a value of no more than 100. As a general principle, however, an organosilicon compound which is a siloxane polymer, is to be regarded as an oligomer for the purpose of this invention as long as it has a shorter siloxane chain length than the final product obtained by the process of the invention. In the preferred polydiorganosiloxanes, each R" denotes a methyl group and $\underline{n}$ has a value of from 10 to 300, more preferably 50 to 150, most preferably from 75 to 100. These polydiorganosiloxanes are produced by hydrolysis and condensation of dihalodiorganosilanes and are commercially available materials.

In the process of the invention silanol end-blocked polydiorganosiloxanes of high viscosity may be produced. If desired, however, condensation products may be end-blocked with triorganosiloxy units. One method of effecting such end-blocking comprises incorporating a triorganoalkoxy silane or a triorganosilanol in the reaction mixture. A more preferred method of producing triorganosiloxy end-blocked reaction polydiorganosiloxanes comprises the incorporation of polydiorganosiloxane materials, which are end-blocked with a triorganosiloxane group at one end and a hydroxyldiorganosiloxane group at the other end. An alternative way is the use of lower molecular weight polydiorganosiloxanes having triorganosiloxane end-groups. This requires usually the use of a catalyst which has some activity in the breaking of the siloxane Si-O-Si bond. Yet another alternative is the use of a silazane, e.g. hexamethyldisilazane. Suitable triorganosiloxane end-blocking units include a wide variety of materials, e.g. trimethylsiloxane, triethylsiloxane, dimethylvinylsiloxane and dimethylphenylsiloxane.

The preferred process of the invention is suitable for use in the preparation of a variety of organosilicon products by a condensation reaction. If desired there may be included with the organosilicon compound other organosilicon compounds for example alkoxysilanes which are reactive with the silanol-containing reagent or condensation products to provide organofunctional or chain terminating groups. Examples of such silanes are trimethyl methoxy silane, methyl phenyl dimethoxy silane, methyl phenyl vinyl ethoxysilane and aminopropyl trimethoxy silane. Instead of incorporating end-blocking reagents in the reaction mixture at the inlet means of the reaction chamber, as described above, it is possible to incorporate these reagents by using them as the fluid which is introduced through the porous wall of the reaction chamber.

The preferred process of the invention involves contacting the organosilicon compounds, which are monomers or oligomers, with a catalyst at a temperature at which the desired rate of polymerisation occurs. It is preferred for the production of polysiloxane materials that the temperature employed is in the range of from about 30°C to about 300°C. Reactions at lower temperatures are normally too slow to be of commercial interest. More preferably the polymerisation reaction is carried out at a temperature of from 50 to 200°C, most preferably 70 to 180°C. It is also preferred that the by-product formed during the condensation reaction is removed. This will cause the acceleration of the reaction and is suitably achieved by the use of an extraction system.

Sufficient catalyst is employed to achieve the desired rate of condensation, having regard to the nature and geometry of the processing equipment, the temperature of the process and other factors, e.g. the residence time of the reaction mixture in the reaction chamber. In most cases it is preferred to employ from 0.001 to 5% by weight of the catalyst based on the weight of the organosilicon compounds in the reaction mixture.

Preferred catalysts are well known condensation catalysts which have been described in a number of publications. Some catalysts will promote condensation reactions, but also act as equilibration catalysts. These

are exemplified by sulphuric acid, hydrochloric acid, Lewis acids, sodium hydroxide, tetramethylammonium hydroxide, tetrabutyl phosphonium silanolate and amines. Such catalysts, though not preferred, are useful provided the presence of low molecular weight species in the final product is not to be avoided, or provided the catalyst is inactivated prior to the rearrangement of polymers. More preferred are condensation specific catalysts. These include dodecylbenzene sulphonic acid, n-hexylamine, tetramethylguanidine, carboxylates of rubidium or caesium, hydroxides of magnesium, calcium or strontium and other catalysts as are mentioned in the art, e.g. in G.B. patent specifications 895 091, 918 823 and E.P. specification 382 365. Also preferred are catalysts based on phosphonitrile chloride, for example those prepared according to U.S. patent specifications 3,839,388 and 4,564,693 or E.P. application 215 470 and phosphonitrile halide catalysts having the general formula $[X(PX_2=N)PX_3]^+[MX_{(v-t+1)}R'_t]^-$, wherein X denotes a halogen atom, M is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, R' is an alkyl group having up to 12 carbon atoms, $\underline{n}$ has a value of from 1 to 6, $\underline{v}$ is the valence or oxidation state of M and $\underline{t}$ has a value of from 0 to $\underline{v}$-1.

Termination of the polymerisation reaction, if desired, may be achieved by conventional and well known methods. For example, the temperature of the reaction mixture may be lowered beyond the point where the catalyst is active. Alternatively, the reaction mixture may be heated to a point where the catalyst is inactivated, e.g. by decomposition, provided the polymer is not affected by such action. Yet another alternative termination procedure is the introduction of an inactivation agent when the polymer has reached its desired degree of polymerisation. This will depend on the type of catalyst used, and may be a neutralisation agent where the catalyst is acidic or alkaline. Suitable neutralisation agents include amines, epoxy compounds and mild acid materials. Where the catalyst is a solid material, or is supported on a solid structure, removal of the catalyst, e.g. by filtration may be used to terminate the reaction.

The condensation products of the process of the invention may vary in viscosity depending on the polymerisation circumstances. The process according to the invention is capable of producing very high viscosity polymers, e.g. of 1,000,000 mm²/s or more, preferably up to about 500,000 mm²/s. Resulting polymers are useful in a number of applications as is well known in the art of organosilicon compounds. Examples of suitable applications include treatment of textile to render them water repellant, paper coating to impart high release surfaces, manufacture of sealant and adhesive products and production of elastomer-forming compositions.

There now follows the description of a specific embodiment of the reactor, which is to be read in conjunction with the drawings. Also given are examples of the process in which all parts and percentages are expressed by weight, unless otherwise indicated.

Figure 1 gives a schematic view of a reactor according to the invention.

Figure 2 gives a cross-sectional view at X_ _X through the reaction chamber.

Figure 3 gives a detailed schematic view of the inlet means and atomising head.

Figure 4 shows a detailed schematic view of an alternative inlet means, having a conically shaped baffle.

The exemplified reactor (10) consists of an inlet means (20), a reactor chamber (30), having a porous wall (31), a jacket means (40) and an outlet means (50). The inlet means (20) comprises a compressed air supply (21) which passes compressed air from a compressor (not shown) through a heat exchanger (also not shown). A second compressed air supply (22) is linked to an atomising device (23) which in this case is a two-fluid nozzle. Also linked to the atomising device (23) is a supply line for the reaction mixture (24) which has a mixing device (25) installed along the line for mixing in a catalyst at the required proportions. In an alternative arrangement (Figure 4) the inlet means has a mixing device (25) for introducing a catalyst to the oligomers/monomers which are fed via a supply line (24) to a small chamber (26) provided with an open truncated conically shaped baffle (27), which causes the reaction mixture to be thoroughly mixed. A compressed air line (21) is feeding into the small chamber (26). A reaction chamber (30) has an internal diameter of 40mm, and a total length of 4000mm. It comprises a porous cylindrical wall (31), which is substantially straight and is positioned vertically with the inlet at the upper end. The porous wall is made from sintered polypropylene and has a permeability of 20 nPm (Fig. 4) or from ceramic with a permeability of 3 nPm (Figs 1-3). Surrounding the porous wall (31) is a jacket means(40) which is divided in three portions (41, 42, 43) each of which surrounds roughly one third of the porous wall. Each of the portions of the jacket means are linked to a fluid supply (44) which may be set at different pressure for each of the portions. The fluid supply is linked via a pump to a container for a liquid (not shown). The outlet means (50) comprises an inlet for a neutralisation agent (51) a de-aeration tank (52), to which is linked an extraction system (53), a filtration system (54) and a drum-off point (55).

In use the catalyst and monomers/oligomers are mixed and fed into the atomiser, together with some compressed air, or fed into the mixing chamber with the conically shaped baffle. A separate supply of heated compressed air forces the atomised or mixed mixture (28) to foam (29) and be pushed down the reaction chamber, while a supply of oligomers are fed separately from the jacket means through the porous wall into the reaction chamber. At the outlet means of the reactor, a mixture in foam-like consistency of the reaction product and compressed air is mixed with a neutralisation agent. The mixture is then filtered and de-aired, and collected

in drums.

Example 1

A production run of polydimethylsiloxane was made using the reactor with the mixing means as exemplified in Figure 4. The process being a continuous polymerisation parameters were varied during a six hour run, as indicated in Table I. As oligomer, fed through line (24) (Oligomer A) was used three α,w-hydroxyl end-blocked polydimethylsiloxane polymer, having a viscosity of 90, 120 or 240 mm²/s respectively, as indicated in the Table. The flow rate is given as Flow in kg of oligomer per hour. Compressed air was fed through line (21) and is given as Air Flow in normal cubic meters per hour at 1 bar and 25°C (Nm³/h). The catalyst employed was dodecylbenzene sulphonic acid (DBSA), given in % by weight based on the amount of Oligomer A in the Table. 9 samples were taken at different times throughout the run (indicated as Time in minutes in the Table) and the corresponding parameters are given in the Table. As oligomer fed through the porous wall, via line (44), was used a α,w-hydroxyl end-blocked polydimethylsiloxane polymer having a viscosity of about 10,000 mm²/s, at a rate of 5kg per hour over the total surface of the reactor chamber. The viscosity of the final polymer (Product) was measured, given in 1000 x mm²/s in the Table. A gas permeation chromotographic (GPC) analysis indicated that the Product was homogeneous. The catalyst was neutralised with ethylene diamine.

TABLE I

Sample	1	2	3	4	5	6	7	8	9
Time	60	105	150	195	240	285	300	310	315
Oligomer A									
Flow	59	59	59	59	59	59	71	70	70
Viscosity	240	240	120	120	90	90	90	90	90
Air Flow	112	112	112	122	119	126	133	225	40
DBSA %	4	4	4	4	4	4	4.8	4.8	4.8
Product									
Viscosity	44	46	43	42	37	38	21	19	15

It is clear from Table I that an increase in the initial viscosity of the linear low molecular weight oligomer feed through line (24) (Figure 4) from 90 to 240 mm²/s provided a product variation in viscosity from 37,000 to 46,000 mm²/s. From the GPC analysis it was clear that only small differences in the polymers occurred. This indicates that the residence time in the reactor was constant for long periods of time and implies that a constant flow was produced in the reactor as a result of the constant quality of porous wall surface (31), produced by backflushing the surface with medium viscosity siloxane oligomers. Inspection of the apparatus after the run revealed that the reactor surfaces were clean and no build up of high viscosity polymer had occurred.

Example 2

A polymerisation run of siloxane materials was carried out on the reactor as described in Figures 1 to 3. The length of the reactor (30), from the point where the reagents were injected to the outlet means (50) was about 4 metres. The process is a continuous polymerisation and reaction conditions were allowed to settle before results were measured. Airflow through line (21) was 160 Nm³/hour, this air was heated to a temperature of about 170°C. Airflow through line (22) was 17 Nm³/hour of cold air used to atomise the oligomer, fed through line (24). This oligomer was a α,w-hydroxyl end-blocked polydimethylsiloxane polymer, having a viscosity of 100 mm²/s, which was fed at a rate of 140 kg/hour. The catalyst employed was an antimony derivative of a phosphonitrile chloride, used in amounts as indicated in Table II in parts by weight per million parts of the oligomer (ppm). The catalyst was supplied as a solution in CH_2Cl_2. The temperature of the incoming oligomer (T_{In}) was varied and this, as well as the outgoing temperature (T_{out}), is recorded in Table II. The resulting rate of polymerised material produced was about 0.145 Nm³/hour. As oligomer fed through the porous wall, via line (44), was used a α,w-hydroxyl end-blocked polydimethylsiloxane polymer having a viscosity of about 10,000 mm²/s, at a rate of 5kg per hour over the total surface of the reactor chamber. The viscosity of the final polymer (Product) was measured, given in 1000 x mm²/s in Table II. A gas permeation chromotographic (GPC) analysis

indicated that the Product was homogeneous having a polydispersity of no more than 2. The catalyst was neutralised with trihexylamine.

TABLE II

Sample	Catalyst (ppm)	T_{in} (°C)	T_{out} (°C)	Viscosity (mm^2/s x 1000)
1	22.50	109	102.6	4.3
2	44.16	150	124.6	306.0
3	22.50	119	105.8	8.1
4	22.50	129	109.2	13.4
5	22.50	139	113.6	21.8
6	22.50	150	117.8	34.0
7	22.50	147	122.9	85.5
8	10.50	148	124.6	3.1
9	13.50	148	125.6	19.3
10	17.25	148	125.9	42.0
11	21.00	148	125.3	75.0
12	24.00	148	125.1	116.0
13	27.75	149	124.8	160.0
14	29.95	149	124.9	204.0
15	32.86	149	124.9	230.0
16	36.51	149	124.9	279.0
17	40.16	150	124.6	306.0
18	43.50	160	130.0	404.0
19	47.00	150	124.0	332.0

It is clear from Table II that an increase in the amount of catalyst used provided a product variation in viscosity from 3,100 to 404,000 mm^2/s. From the GPC analysis it was clear that the product had a good degree of monodispersity. Inspection of the apparatus after the run revealed that the reactor surfaces were clean and no build up of high viscosity polymer had occurred.

Claims

1. A continuous static polymerisation reactor for the production of liquid polymers which comprises an inlet means (20), an elongated hollow reaction chamber (30), a jacket means (40) spaced from and in surrounding relationship to said reaction chamber (30), and an outlet means (50) characterised in that the inlet means (20) comprises an atomising device (23), the elongated hollow reaction chamber (30) has a porous wall (31) and the jacket means is provided with means (44) for introducing a fluid through the porous wall (31) into the elongated hollow reaction chamber (30).

2. A reactor according to Claim 1 further characterised in that an inert gas supply (24) is provided to the inlet means.

3. A reactor according to Claim 1 or Claim 2 further characterised in that the reaction chamber (30) is a hollow cylinder having a diameter of from 20 to 250mm and a length of from 250 to 20,000mm, and in that the length is at least twice the size of the diameter.

4. A reactor according to any one of the preceding claims further characterised in that the jacket means (40) is adapted to introduce a liquid through the porous wall (31) of the reaction chamber (30).

5. A reactor according to any one of the preceding claims further characterised in that the outlet means (50) comprises a neutralisation inlet (51), a de-aeration unit (52, 53) or a filtration unit (54).

6. A process for making liquid polymers by condensing monomers and/or oligomers in a polymerisation reactor, comprising the mixing of the monomers and/or oligomers with the appropriate amount of catalyst where required, the mixing of the resultant mixture with a pressurised gas to cause it to reach a foam-like consistency, feeding the foaming mixture through an inlet means into a reaction chamber having a porous wall, feeding a fluid through the porous wall into the reaction chamber in order to avoid build up of the polymer on the wall of the reaction chamber, causing the monomers and/or oligomers to polymerise in the reaction chamber and collecting the polymers at the outlet means of the polymerisation reactor.

7. A process according to Claim 6 further characterised in that the monomers or oligomers are organosilicon compounds having silicon-bonded -OR groups, in which R represent a hydrogen atom or a lower alkyl group having up to 6 carbon atoms, provided at least some R groups are hydrogen, and in that the liquid polymers are polydiorganosiloxane materials.

8. A process according to Claim 7 further characterised in that the organosilicon compounds are α,w-hydroxyl end-blocked polydimethylsiloxanes.

9. A process according to Claim 6 or 7 further characterised in that the polymers are polydimethylsiloxane materials which are end-blocked with diorganosiloxanol groups or with triorganosiloxane groups.

10. A process according to Claim 9 further characterised in that the triorganosiloxane groups are selected from trimethyl siloxane, vinyldimethyl siloxane and dimethyl phenyl siloxane groups.

11. A process according to any one of Claims 6 to 10 further characterised in that the polymerisation reaction is carried out at a temperature of from 30 to 300°C.

12. A process according to any one of Claims 6 to 11 further characterised in that it is carried out in the presence of a catalyst, which is a condensation specific catalyst.

13. A process according to Claim 12 further characterised in that the catalyst is selected from dodecylbenzene sulphonate, n-hexylamine, tetramethylguanidine, carboxylates of rubidium or caesium, hydroxides of magnesium, calcium or strontium, catalysts based on phosphonitrile chloride and phosphonitrile halide catalysts having the general formula $[X(PX_2=N)PX_3]^+[MX_{(v-t+1)}R'_t]^-$, wherein X denotes a halogen atom, M is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, R' is an alkyl group having up to 12 carbon atoms, $\underline{n}$ has a value of from 1 to 6, $\underline{v}$ is the valence or oxidation state of M and $\underline{t}$ has a value of from 0 to $\underline{v}$-1.

14. A process according to any one of Claims 6 to 13 further characterised in that the catalyst is neutralised when the polymer has reached its desired degree of polymerisation.

Patentansprüche

1. Kontinuierlicher statischer Polymerisationsreaktor zur Herstellung von flüssigen Polymeren, umfassend eine Einlaßeinrichtung (20), eine längliche hohle Reaktionskammer (30), einen Mantel (40), der von der Reaktionskammer (30) entfernt ist und diese umgibt, und eine Auslaßeinrichtung (50), dadurch gekennzeichnet, daß die Einlaßeinrichtung (20) eine Zerstäubervorrichtung (23) umfaßt, die längliche hohle Reaktionskammer (30) eine poröse Wand (31) hat und der Mantel mit einer Einrichtung (44) versehen ist, um ein fließendes Medium durch die poröse Wand (31) in die längliche hohle Reaktionskammer (30) einzuführen.

2. Reaktor nach Anspruch 1, weiter dadurch gekennzeichnet, daß die Einlaßeinrichtung mit einer Zuführung für Inertgas (24) versehen ist.

3. Reaktor nach Anspruch 1 oder Anspruch 2, weiter dadurch gekennzeichnet, daß die Reaktionskammer

(30) ein hohler Zylinder mit einem Durchmesser von 20 bis 250 mm und einer Länge von 250 bis 20.000 mm ist und daß die Länge mindestens das Zweifache der Größe des Durchmessers ist.

4. Reaktor nach einem der vorhergehenden Ansprüche, weiter dadurch gekennzeichnet, daß der Mantel (40) so ausgebildet ist, daß eine Flüssigkeit durch die poröse Wand (31) der Reaktionskammer (30) eingeführt werden kann.

5. Reaktor nach einem der vorhergehenden Ansprüche, weiter dadurch gekennzeichnet, daß die Auslaßeinrichtung (50) einen Neutralisierungseinlaß (51), eine Entlüftungseinheit (52, 53) oder eine Filtrationseinheit (54) umfaßt.

6. Verfahren zur Herstellung von flüssigen Polymeren durch Kondensation von Monomeren und/oder Oligomeren in einem Polymerisationsreaktor, umfassend, daß man die Monomeren und/oder Oligomeren mit der geeigneten Menge an Katalysator, falls erforderlich, vermischt, die entstehende Mischung mit einem unter Druck stehenden Gas vermischt, um zu bewirken, daß sie eine schaumartige Konsistenz bekommt, die schäumende Mischung durch eine Einlaßeinrichtung in eine Reaktionskammer mit einer porösen Wand leitet, ein fließendes Medium durch die poröse Wand in die Reaktionskammer führt, um Ablagerungen des Polymers an der Wand der Reaktionskammer zu vermeiden, die Monomeren und/oder Oligomeren in der Reaktionskammer polymerisieren läßt und die Polymere an der Auslaßeinrichtung des Polymerisationsreaktors sammelt.

7. Verfahren nach Anspruch 6, weiter dadurch gekennzeichnet, daß die Monomeren oder Oligomeren Organosiliciumverbindungen mit siliciumgebundenen -OR-Gruppen sind, worin R ein Wasserstoffatom oder eine Niedrigalkylgruppe mit bis zu 6 Kohlenstoffatomen bedeutet, vorausgesetzt, daß mindestens einige Gruppen R Wasserstoff sind, und daß die flüssigen Polymere Polydiorganosiloxanmaterialien sind.

8. Verfahren nach Anspruch 7, weiter dadurch gekennzeichnet, daß die Organosiliciumverbindungen α,ω-Hydroxylpolydimethylsiloxane sind.

9. Verfahren nach Anspruch 6 oder 7, weiter dadurch gekennzeichnet, daß die Polymere Polydimethylsiloxanmaterialien sind, die mit Diorganosiloxanolgruppen oder mit Triorganosiloxangruppen endblockiert sind.

10. Verfahren nach Anspruch 9, weiter dadurch gekennzeichnet, daß die Triorganosiloxangruppen ausgewählt sind aus Trimethylsiloxan-, Vinyldimethylsiloxan- und Dimethylphenylsiloxangruppen.

11. Verfahren nach einem der Ansprüche 6 bis 10, weiter dadurch gekennzeichnet, daß die Polymerisationsreaktion bei einer Temperatur von 30 bis 300°C durchgeführt wird.

12. Verfahren nach einem der Ansprüche 6 bis 11, weiter dadurch gekennzeichnet, daß es in Gegenwart eines Katalysators durchgeführt wird, der ein kondensationsspezifischer Katalysator ist.

13. Verfahren nach Anspruch 12, weiter dadurch gekennzeichnet, daß der Katalysator ausgewählt ist aus Dodecylbenzolsulfonat, n-Hexylamin, Tetramethylguanidin, Carboxylaten von Rubidium oder Caesium, Hydroxiden von Magnesium, Calcium oder Strontium, Katalysatoren auf Basis von Phosphonitrilchlorid und Phosphonitrilhalogenkatalysatoren der allgemeinen Formel $[X(PX_2=N)PX_3]^+[MX_{(v-t+1)}R'_t]^-$, worin X ein Halogenatom bedeutet, M ein Element mit einer Elektronegativität von 1,0 bis 2,0 auf der Pauling-Skala ist, R' eine Alkylgruppe mit bis zu 12 Kohlenstoffatomen ist, n einen Wert von 1 bis 6 hat, v die Valenz oder der Oxidationszustand von M ist und t einen Wert von 0 bis v-1 hat.

14. Verfahren nach einem der Ansprüche 6 bis 13, weiter dadurch gekennzeichnet, daß der Katalysator neutralisiert wird, wenn das Polymer den gewünschten Polymerisationsgrad erreicht hat.

Revendications

1. Réacteur de polymérisation statique en continu pour la production de polymères liquides, comprenant un moyen d'entrée (20), une chambre de réaction creuse de forme allongée (30), un moyen d'enveloppe (40) espacé de et entourant ladite chambre de réaction (30), et un moyen de sortie (50), caractérisé en ce que le moyen d'entrée (20) comporte un dispositif atomiseur (23), la chambre de réaction creuse de

forme allongée (30) possède une paroi poreuse (31) et le moyen d'enveloppe est pourvu de moyens (44) pour introduire un fluide à travers la paroi poreuse (31) dans la chambre de réaction creuse de forme allongée (30).

2. Réacteur selon la revendication 1, caractérisé en ce qu'une alimentation de gaz inerte (24) est prévue pour le moyen d'entrée.

3. Réacteur selon la revendication 1 ou la revendication 2, caractérisé en ce que la chambre de réaction (30) est un cylindre creux avec un diamètre de 20 à 250 mm et une longueur de 250 à 20.000 mm, et que la longueur est d'au moins deux fois le diamètre.

4. Réacteur selon l'une des revendications précédentes, caractérisé en ce que le moyen d'enveloppe (40) est prévu pour introduire un liquide via la paroi poreuse (31) de la chambre de réaction (30).

5. Réacteur selon l'une des revendications précédentes, caractérisé en ce que le moyen de sortie (50) comporte une entrée de neutralisation (51), une unité de désaération (52, 53) ou une unité de filtration (54).

6. Procédé pour fabriquer des polymères liquides en condensant des monomères et/ou des oligomères dans un réacteur de polymérisation, procédé comprenant le mélange des monomères et/ou des oLigomères avec la quantité appropriée de catalyseur lorsque nécessaire, le mélange du mélange résultant avec un gaz sous pression pour lui donner une consistence de mousse, l'amenée du mélange moussé via un moyen d'entrée dans une chambre de réaction présentant une paroi poreuse, l'amenée d'un fluide à travers la paroi poreuse dans la chambre de réaction pour éviter les dépôts de polymère sur la paroi de la chambre de réaction, faisant en sorte que les monomères et/ou les oligomères polymérisent dans la chambre de réaction, et la collecte des polymères au moyen de sortie du réacteur de polymérisation.

7. Procédé selon la revendication 6, caractérisé de plus en ce que les monomères ou les oligomères sont des composés organosilicium avec des groupes -OR fixés sur le silicium, dans lesquels R signifie un atome d'hydrogène ou un groupe alkyle inférieur avec jusqu'à 6 atomes de carbone, à condition qu'au moins quelques groupes R signifient l'hydrogène, et dans lequel les polymères liquides sont des polydiorganosiloxanes.

8. Procédé selon la revendication 7, caractérisé, de plus, en ce que les composés organosilicium sont des polydiméthylsiloxanes à terminaison de chaîne bloquée α,w-hydroxyle.

9. Procédé selon les revendications 6 à 7, caractérisé, de plus, en ce que les polymères sont des polydiméthylsiloxanes à chaîne terminée bloquée par des groupes diorganosiloxanol ou des groupes triorganosiloxane.

10. Procédé selon la revendication 9, caractérisé, de plus, en ce que les groupes triorganosiloxane sont choisis parmi les groupes triméthylsiloxane, vinyldiméthylsiloxane et diméthylphénylsiloxane.

11. Procédé selon l'une des revendications 6 à 10, caractérisé, de plus, en ce que la réaction de polymérisation est effectuée à une température de 30 à 300°C.

12. Procédé selon l'une des revendications 6 à 11, caractérisé, de plus, en ce qu'il est exécuté en présence d'un catalyseur qui est un catalyseur spécifique de condensation.

13. Procédé selon la revendication 12, caractérisé, de plus, en ce que le catalyseur est choisi parmi le groupe comportant le dodécylbenzènesulfonate, la n-hexylamine, la tétraméthylguanidine, les carboxylates de rubidium ou de césium, les hydroxydes de magnésium, de calcium ou de strontium, des catalyseurs à base de chlorure de phosphonitrile et des catalyseurs d'halogénure de phosphonitrile répondant à la formule générale $[X(PX_2=N)PX_3]^+[MX_{(v-t+1)}R't]$, où X désigne un atome d'halogène, M est un élément possédant une électronégativité de 1,0 à 2,0 selon l'échelle de Pauling, R' est un groupe alkyle présentant jusqu'à 12 atomes de carbone, n possède une valeur de 1 à 6, v est la valence ou l'état d'oxydation de M et t a une valeur de 0 à v-1.

14. Procédé selon l'une des revendications 6 à 13, caractérisé, de plus, en ce que le catalyseur est neutralisé lorsque le polymère a atteint le degré de polymérisation désiré.

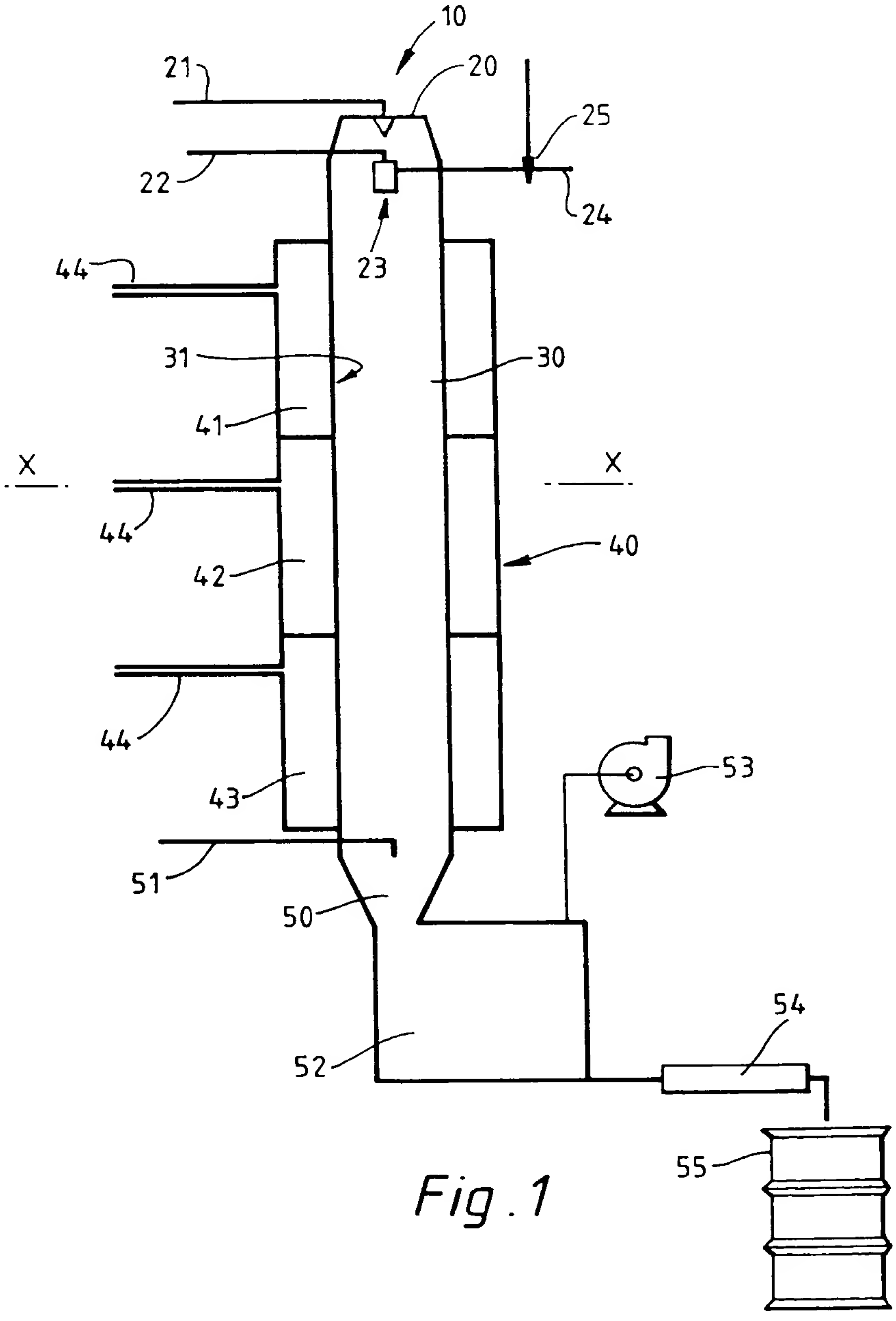

Fig. 1

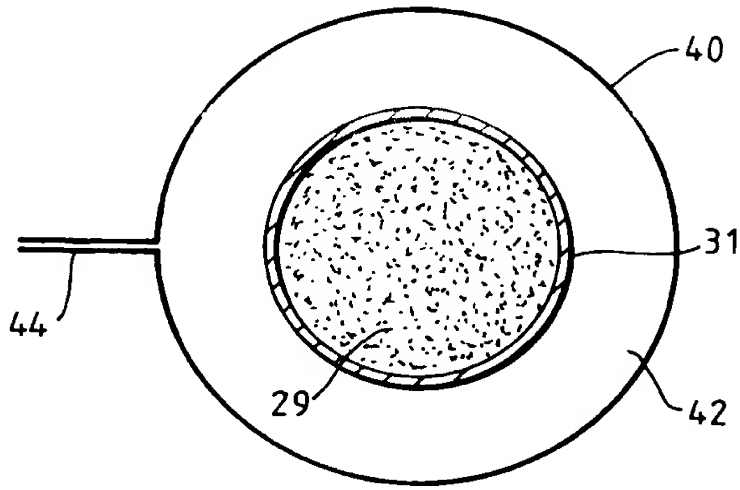

Fig. 2

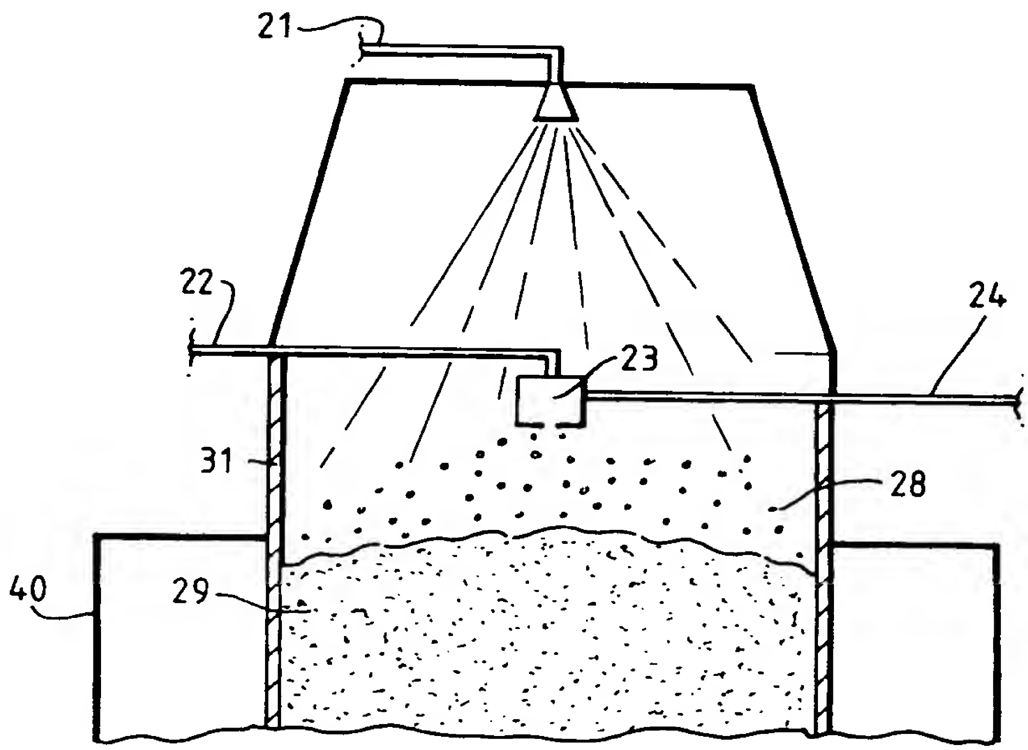

Fig. 3

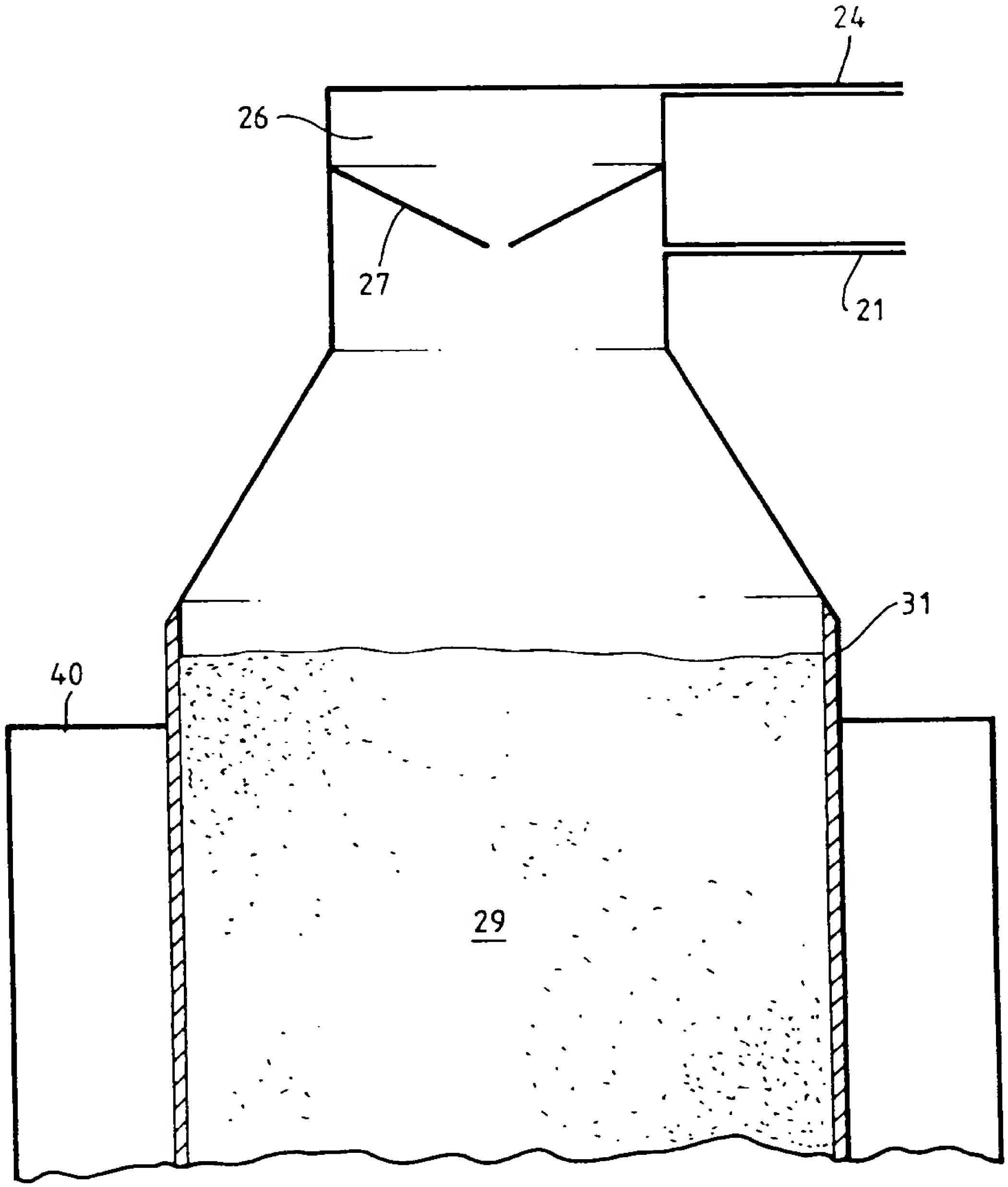

Fig. 4